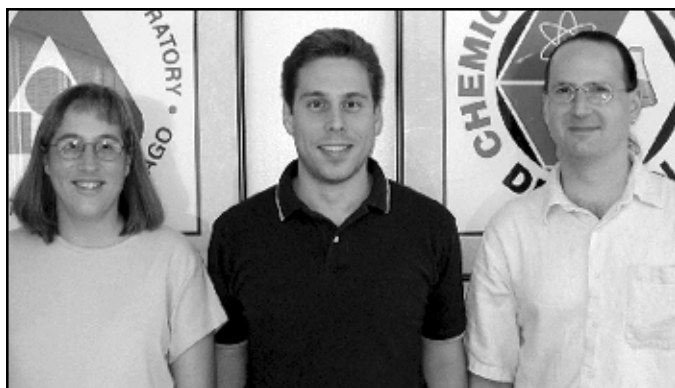


Solid Oxide Fuel Cell Research and Development



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Objectives

- Develop solid oxide fuel cell (SOFC) cathode formulations that are effective at $\leq 800^\circ\text{C}$ and are compatible with electrolytes based primarily on yttria-stabilized zirconia (YSZ), but also on gadolinia-doped ceria.
- Develop SOFC anode materials that can be used with sulfur-containing fuel gases with little or no degradation in fuel cell performance.
- Identify and/or develop metal or metal-ceramic materials for use as effective, low-cost bipolar plates in SOFCs operating at $\leq 800^\circ\text{C}$.

Key Milestones

- Achieved $0.15 \Omega \text{ cm}^2$ cathode area specific resistance (ASR) at 800°C using a lanthanum strontium ferrite as compared to $70 \Omega \text{ cm}^2$ for the standard lanthanum strontium manganite cathode.
- Demonstrated severe poisoning of Ni-YSZ anode at 5-30 ppm H_2S ; no poisoning of Pt anode.
- Identified and synthesized several potentially sulfur-tolerant anode materials; electrochemical testing is underway.
- Demonstrated corrosion and scale resistances for laboratory-prepared chromium and non-chromium-containing alloy bipolar plates similar to best commercially-available wrought materials; a few non-chromium-containing materials showed promising ASRs.
- Developed a novel processing approach that easily permits layered metallic bipolar plates of graded composition and a range of flow field designs.

Approach

Cathodes: The traditional cathode material for high temperature (1000°C) SOFCs is lanthanum strontium manganite (LSM). At temperatures of 800°C and below, the LSM cathode suffers from poor electrochemical performance due to its limited oxygen ion conductivity. Our approach to develop a better-performing low temperature cathode is to develop materials with both high ionic and electronic conductivity at $\leq 800^\circ\text{C}$. Avenues we are exploring are replacing the manganese in LSM with cobalt, iron, or nickel, and moving to materials with alternative structures. These include materials with the K_2NiF_4 structure, layered structures (e.g., $\text{YBa}_2\text{Cu}_3\text{O}_7$), composite materials (LSM + YSZ), pyrochlores ($\text{A}_2\text{B}_2\text{O}_5$), brownmillerites ($\text{A}_2\text{B}_2\text{O}_7$), and spinels. Potential cathode materials are systematically screened on zirconia- and ceria-based electrolytes at various temperatures using impedance spectroscopy. Long-term interaction experiments between the cathode materials and the electrolytes are used to determine material compatibility. Promising

candidates are further characterized and tested, first as half-cells and then as full cells.

Sulfur-Tolerant Anodes: Nickel-YSZ cermet is the most common anode material used in SOFCs because it exhibits good catalytic activity for the electrochemical oxidation of hydrogen, high electrical conductivity, and a thermal expansion coefficient that is well matched to that of the electrolyte. However, as little as 1 ppm H_2S in the fuel gas causes a $\sim 10\%$ drop in cell voltage at 900°C , with the performance degradation becoming even more pronounced at lower temperatures [1, 2]. Evidently, sulfur from H_2S gets adsorbed on the active sites on the nickel, thereby making those sites unavailable for hydrogen electro-oxidation. We are exploring three approaches to developing sulfur-tolerant anodes for SOFCs. The first approach is to modify the Ni-YSZ cermet anode by use of an additive that has suitable redox chemistry. The additive would capture sulfur from the fuel stream at rates and affinities greater than the ones for sulfur adsorption on nickel. The captured sulfur would then be oxidized to SO_2 , either electrochemically or thermally, to regenerate the starting material. The second approach is to replace the Ni phase in Ni-YSZ cermet anode with other metals or metal alloys that are active toward the electrochemical oxidation of H_2 but are inert to sulfur poisoning. The third approach is to investigate new classes of materials based on carbides and/or sulfides. The candidate materials are sintered onto YSZ electrolyte and their electrochemical performance is tested in hydrogen, simulated reformat, and hydrogen spiked with 5 to 30 ppm H_2S using a half-cell configuration equipped with a reference electrode.

Bipolar Plates: Lanthanum chromite and strontium-doped lanthanum chromite are the standard materials used as bipolar plates for SOFCs operating at 1000°C . As the operating temperature of the fuel cell is decreased, expensive ceramic interconnects can be replaced by inexpensive metallic materials such as iron-based alloys. An effective bipolar plate must be dense, stable, and electrically conductive in both oxidizing and reducing environments in the operating temperature range of the SOFC ($600\text{--}800^\circ\text{C}$). The material's coefficient of thermal expansion (CTE) must also closely match the CTE of the other materials in the SOFC to avoid excessive residual thermal stresses that could result in mechanical failure. Two approaches are

being examined in this project. The first is to examine the properties of a number of materials to identify those that offer the best chance of success as a bulk material, including composites. The second is to explore the concept of a substrate with a suitable coating material in case a single material meeting all the desired criteria cannot be found. A bulk material would be self-healing if anything were to happen to the protective layer. Coated materials could be used for materials that are not easily processed or are too expensive in bulk. The coating approach also allows bipolar plates to be coated on each side with a material best suited for either the cathode or anode conditions.

Results

Cathodes: We are investigating replacing the manganese in the traditional perovskite cathode material (LSM) with cobalt, nickel, or iron, as well as materials other than perovskites. As shown in Figure 1, we have found that the ferrite-based perovskites display the best cathode performance over the entire temperature range of interest ($650\text{--}800^\circ\text{C}$). Of these, lanthanum strontium ferrite (LSF) has proven the most compatible and best-performing single-phase cathode material. Further, the area-specific resistance (ASR) of LSF was found to stabilize within the first 50 hr at 800°C and then remain constant up to at least 500 hr, confirming chemical and physical stability of the material under use.

While stoichiometric LSF was found to be a better cathode than LSM, it did not possess a low enough ASR at $\leq 800^\circ\text{C}$ to be a usable cathode. Small A-site deficiencies (2%), often used in LSM and other perovskite cathodes to prevent reaction with the electrolyte, did not improve LSF, probably because LSF does not show reaction tendencies with YSZ. As shown in Figure 2, we have found that heavy A-site deficiencies (5–20%) dramatically improve the cathode performance, with 10% deficiency being optimum. The 20% La-deficient cathode had a small secondary phase present, which probably explains why no further improvement was obtainable with this cathode. In a separate study looking at the effect of Sr content, we found 25 mol% Sr doping in stoichiometric LSF achieved the lowest ASR and decided to test a La-deficient cathode with 25 mol% Sr doping ($\text{La}_{0.7}\text{Sr}_{0.25}\text{FeO}_3$). Our lowest ASR to date of $0.15\ \Omega\text{cm}^2$ was achieved

with this material. We postulate that the performance improvements observed with A-site deficiency are due to alterations in the defect chemistry of LSF, which cause the formation of both oxygen vacancies and electronic carriers leading to overall improvements in the total conductivity. Further improvements in ASR may come from additional doping on the B-site. As seen in Figure 2, 20 mol% doping of Co on the B-site improved the performance of stoichiometric LSF.

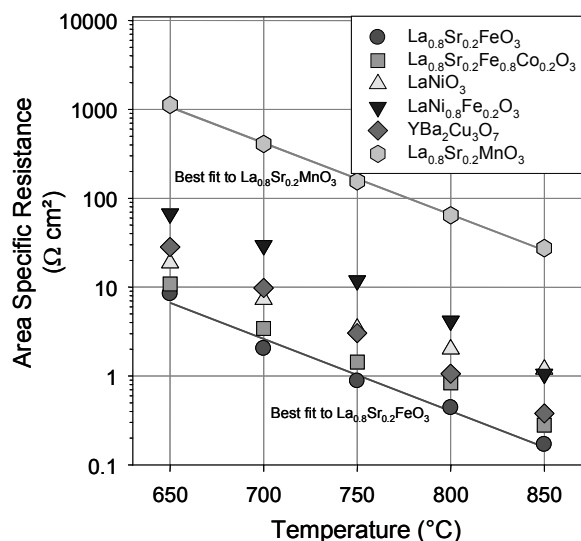


Figure 1. Area specific resistances of cathode materials developed at Argonne compared to the traditional lanthanum strontium manganite.

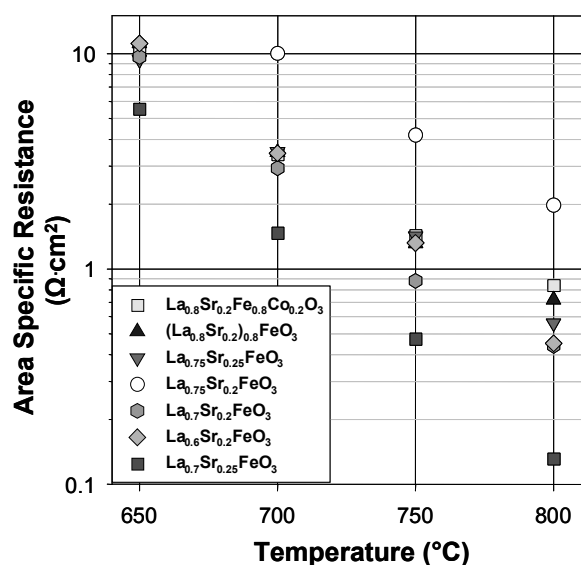


Figure 2. Area specific resistances of various stoichiometric and A-site deficient LSF cathode materials.

Sulfur-Tolerant Anodes: We have verified the performance loss of a conventional Ni-YSZ anode in sulfur-containing fuel using an electrochemical half-cell equipped with a reference electrode. As shown in Figure 3, the anode over-potential on Ni-YSZ increases by 130 mV at a cell current of 500 mA/cm² with 5 ppm H₂S in the fuel stream and by >600 mV with 30 ppm H₂S in the fuel stream. However, a platinum anode shows no increase in anode over-potential with addition of H₂S due to the lower sulfur affinity of platinum (i.e., lower adsorption energy) as compared to nickel.

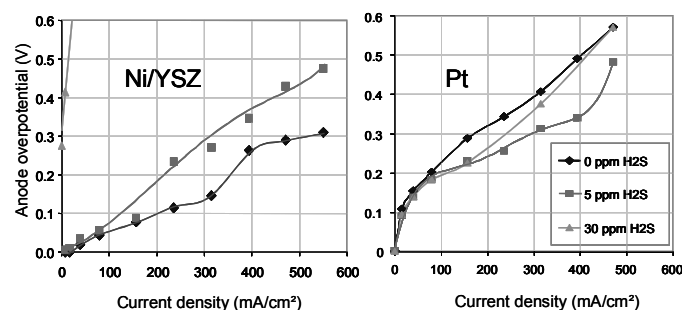


Figure 3. Anode over-potentials for Ni/YSZ and Pt anodes at 800°C in humidified reformate and reformate spiked with 5 and 30 ppm H₂S.

We have synthesized several half-cells with novel anode compositions based on redox active materials that preferentially adsorb and oxidize sulfur, alloys that lower the adsorption energy of sulfur on the anode, and carbides or sulfides capable of oxidizing hydrogen. The electrochemical performances of anodes comprised of a Ni/Ag-YSZ cermet and of a Ni/Ceria-YSZ cermet have been determined on pure hydrogen and hydrogen containing 5 ppm H₂S. As shown in Figure 4, the Ni/Ag-YSZ cermet has a lower over-potential and the Ni/ceria-YSZ cermet has a higher over-potential for hydrogen oxidation than the conventional Ni-YSZ cermet anode. Both of these anodes exhibited degradation in electrochemical performance with as little as 5 ppm H₂S in the hydrogen stream. Efforts are underway to quantify the magnitude of this degradation and to determine its reversibility.

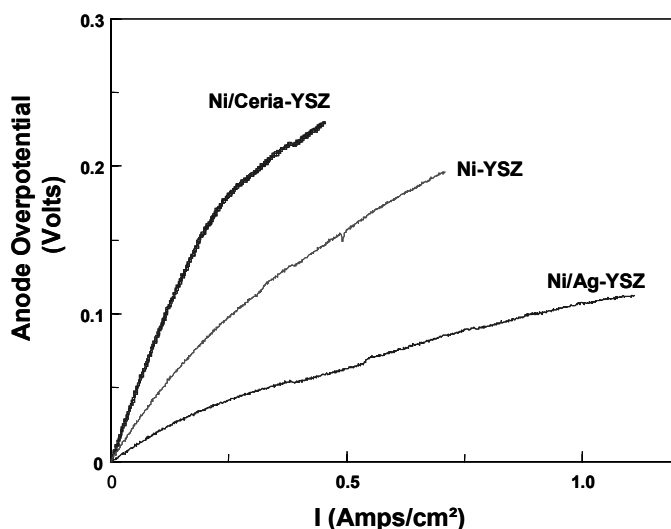


Figure 4. Anode over-potentials for Ni/Ceria-YSZ, Ni-YSZ, and Ni/Ag-YSZ at 800°C in humidified hydrogen.

Bipolar Plates: The initial work in bipolar plate development looked at the weight gain and electrical resistance of a number of different alloys. Figure 5 provides a graphical representation comparing the weight gain for a number of different alloys that were treated in humidified air for 400 hours. Commercially-available materials (Group 1), are compared to ANL-fabricated modified ferritic stainless steel compositions (Group 2), and ANL-fabricated ferritic steels without chromium (Group 3). The commercially-available wrought materials typically show a low weight gain with the E-Brite material having the lowest weight gain. The materials produced at Argonne by powder metallurgy and tape casting typically have higher weight gains, an inherent difference between powder metallurgy and wrought materials. The alloys with chromium show much lower weight gains than those without, a result of a more protective chromium oxide scale. Figure 6 provides a graphical representation of the ASRs of the same materials. Here it can be seen that the commercially-available materials typically have higher ASR values than similar alloys produced by tape casting. While the wrought materials showed lower weight gains, their oxide scales typically had higher resistances. The materials prepared without chromium typically had very high ASR values, associated with high weight gains. However, a couple of the alloys showed low weight gains and relatively low ASR values, attributed to lower resistance of the oxide scale. The research on

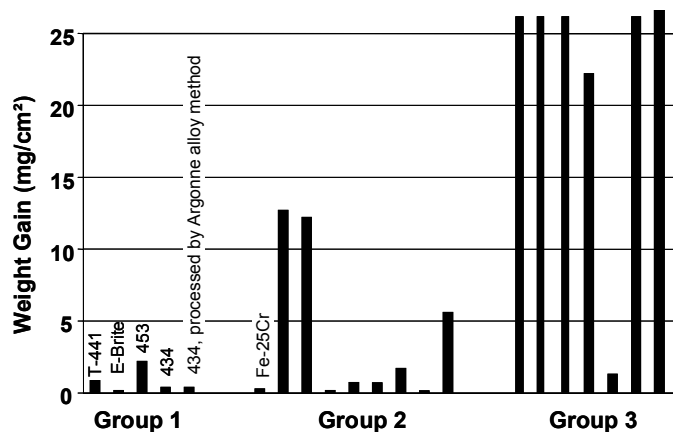


Figure 5. Weight gain of bipolar plate alloys after 400 hours in humid air at 800°C. Group 1: commercially-available alloys, Group 2: ANL ferritic stainless steel compositions, Group 3: ANL iron alloys without chromium.

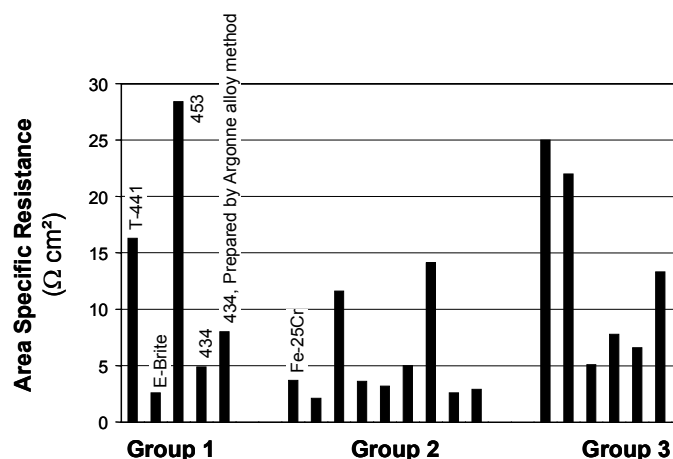


Figure 6. Area specific resistances of bipolar plate alloys after 400 hours in humid air at 800°C. Group 1: commercially-available alloys, Group 2: ANL ferritic stainless steel compositions, Group 3: ANL iron alloys without chromium.

alloy development has produced a couple of novel ferritic stainless steels with properties slightly superior to commercial E-Brite for this application and some novel alloys that do not contain any chromium that show promise. Though the Argonne alloys show improvements over the best commercially-available materials, improvements are needed in the conductivities to reach the target ASR of less than 25 mΩ cm².

One advantage of using a powder processing approach is that functionally graded materials can be easily made. One of the better novel alloy compositions was prepared on a cheaper 434 material. The weight gain and ASR values after exposure to humidified air

were determined for the 434, the alloy, and the 434 clad with the alloy. The results show that the functionally graded material had properties of interest similar to the bulk alloy and superior to the 434. Energy dispersive x-ray analysis of the composite showed that key alloying elements did not migrate into the 434 during processing within the detection limit of this technique. This type of processing would allow for a bipolar plate material to be made easily with different alloys designed to meet the specific requirements of each environment. A good example would be using a non-chromium containing alloy on the cathode side of the interconnect, where chromium poisoning is a concern, and a chromium containing alloy on the anode side, where chromium does not appear to have any effect. This process allows the minimization of expensive alloying elements by placing them only where they are needed, while the bulk of the bipolar plate can then be of a lower cost material and/or be tailored to minimize thermal stresses across the bipolar plate and the fuel cell. Another advantage of

this processing technique is a range of flow channels or flow field designs can easily be incorporated into the bipolar plate structure. Figure 7 shows a few possible variations on this idea produced using this approach. All of these designs were produced in the green state so that no secondary fabrication processing was needed, which could result in a reduction in fabrication costs. The sizes, shapes, designs, and orientations of the flow fields can easily be tailored to specific design requirements.

Conclusions

Cathodes: Several potential low-temperature cathode materials have been developed based on the idea of maximizing the cathodes' ionic and electronic conductivity at temperatures $\leq 800^\circ\text{C}$. Lanthanum strontium ferrites showed the best cathode performance at $\leq 800^\circ\text{C}$. A cathode performance of $0.15 \Omega \text{ cm}^2$ was achieved with an LSF at 800°C as compared to $70 \Omega \text{ cm}^2$ for the standard high temperature lanthanum strontium manganite cathode. We have found the best LSF performance with 10 mol% lanthanum deficiency on the A-site of the perovskite and 25 mol% strontium doping. In the future, we plan to explore other compositions (e.g., additional doping on the B-site of the non-stoichiometric LSF) and to optimize the cathode microstructure to achieve ASRs of $< 0.2 \Omega \text{ cm}^2$ at temperatures below 800°C .

Sulfur-Tolerant Anodes: We have demonstrated that the conventional Ni-YSZ anode is severely poisoned by 5-30 ppm H_2S in either hydrogen or reformate fuel. Under identical conditions, a Pt anode was not poisoned. We found better electrochemical performance for a Ni/Ag-YSZ cermet anode as compared to Ni-YSZ in hydrogen gas, however, this electrode showed degradation in performance with H_2S present. The magnitude of this degradation is being determined. Future work will include electrochemical testing of several half-cells with novel anode compositions based on redox active materials that preferentially adsorb and oxidize sulfur, alloys that lower the adsorption energy of sulfur on the anode, and carbides or sulfides capable of oxidizing hydrogen.

Bipolar Plates: A number of different iron-based alloys have been prepared using a combination of mechanical alloys and tape casting techniques. Some

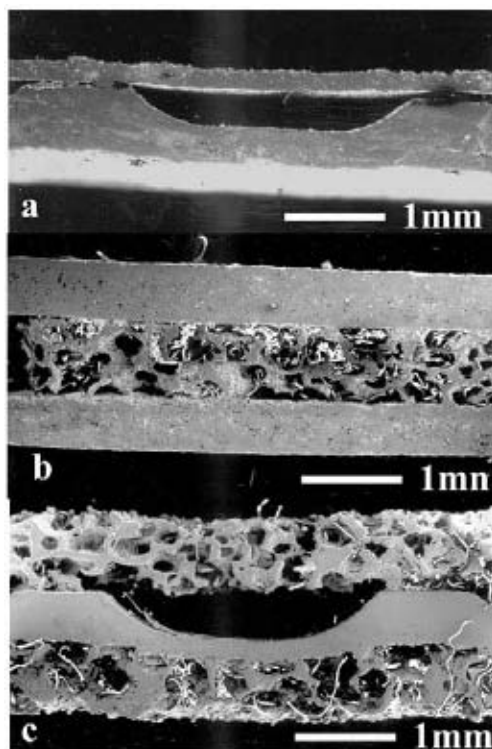


Figure 7. SEM micrographs of a few different types of metallic bipolar plate structures possible using the Argonne processing technique.

alloys have demonstrated corrosion and scale resistances similar to the best commercially-available wrought materials. Alloys have also been prepared without chromium, and while the properties are not as good as the chromium-containing alloys, some show promise. Presently more work on characterizing the oxide scale is underway. This will be used to help produce the next generation of alloys. We have demonstrated that the bipolar plate processing technique developed at Argonne is a practical means for producing a functionally-graded material. As alloys develop, the best alloys for both the anode and cathode conditions will be prepared, tested, and incorporated into a functionally graded design. The Argonne process has proven to be very flexible in producing a range of bipolar plate flow field configurations.

References

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2. Y. Matsuzaki and I. Yasuda, *Solid State Ionics*, 132, 261-269 (2000).